

Diesel soot combustion ceria catalysts[☆]A. Bueno-López^{*}

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ABSTRACT

Different aspects of the ceria-catalyzed Diesel soot combustion reactions have been critically discussed, such as the high catalytic activity of ceria for Diesel soot combustion in comparison to some other potential catalysts, the potential ceria-catalyzed Diesel soot combustion mechanisms (the so-called NO₂-assisted mechanism and the active oxygen mechanism) and the effect of ceria doping with suitable cations like those of Pr, La or Zr. Ceria must be doped in order to enhance thermal stability, but ceria doping also changes different physicochemical and catalytic properties of ceria. Zr-doping, for instance, has a double role on ceria as soot combustion catalyst: enhances ceria oxidation capacity of the adsorbed NO_x species (positive effect) but stabilizes NO₂ on surface (negative effect). The surface properties of a ceria catalyst are usually more important than those of bulk: high surface area/small crystal size usually has a positive effect on the catalyst performance and, in mixed oxides, the surface composition also plays a role. The optimal dopant loading depends on the foreign cation being, for instance, around 5–10%, 20–30% and 50 mol% for La³⁺, Zr⁴⁺, and Pr^{3+/4+}, respectively.

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1. The problem

Soot particles are formed as undesired by-products in combustion process, being one of the main pollutants emitted by Diesel engines together with NO_x, CO and unburned hydrocarbons [1]. Typical gas exhaust composition of a Diesel car, which is summarized in Table 1, is 30–80 ppm hydrocarbons, 200–1500 ppm CO, 300–1650 ppm NO (~0 ppm NO₂), 5–18% O₂, >2% H₂O and >2% CO₂.

Soot particles consist of a carbon nucleus with some inorganic material and adsorbed hydrocarbons, SO_x, and water [2]. Fig. 1 shows TEM images of a real soot sample. The single particles of few nanometers present an amorphous core surrounded by a graphitic shell, and such single particles agglomerate in larger entities with size typically in the range 0.1–10 μm [3].

Several adverse effects on health have been attributed to soot. A fraction of these particles (the so-called PM-10, with size smaller than 10 μm) can penetrate the respiratory tract and are deposited on lungs increasing cancer risk, asthma and bronchitis. The adsorbed hydrocarbons are mutagenic substances and SO_x in contact with water form strong acid compounds.

Diesel particle traps with different designs can be used for soot removal from gas streams, wall-flow monoliths being the most popular [3,4]. Fig. 2 shows a commercial SiC Diesel Particulate Filter (DPF). The structure of this type of filters is similar to that of honeycomb monoliths, but with 50% of the channels plugged in one side of the piece and the remaining channels plugged in the opposite side. The gas stream is allowed to enter into the filter only through the open channels of the exposed side, and goes through the porous walls while soot particles get stuck on the walls. Finally it leaves the filter by a neighboring channel. The preferred materials to manufacture DPF filters are cordierite (2MgO·2Al₂O₃·5SiO₂) and SiC, because they are able to support the demanding thermal conditions of the regeneration steps. There have been reported temperature gradients of 100 °C/cm along both radial and longitudinal directions of DPFs [5]. Important differences in physical properties between cordierite and SiC are their melting temperatures (~1400 and ~2700 °C, respectively) and their expansion coefficients (2.0 × 10^{−6} and 4.3 × 10^{−6} from 25 to 800 °C, for cordierite and SiC respectively). Due to these differences SiC is able to support the high temperatures reached during filters regeneration better than cordierite but is more prone to suffer damages due to thermal shock. Large SiC filters, as those used in Diesel cars, are made of several pieces glue together in order to improve the thermal shock resistance (see Fig. 2) while cordierite filters can be made in single pieces.

Once soot is collected on a filter different regeneration strategies can be applied. The thermal combustion of Diesel soot usually

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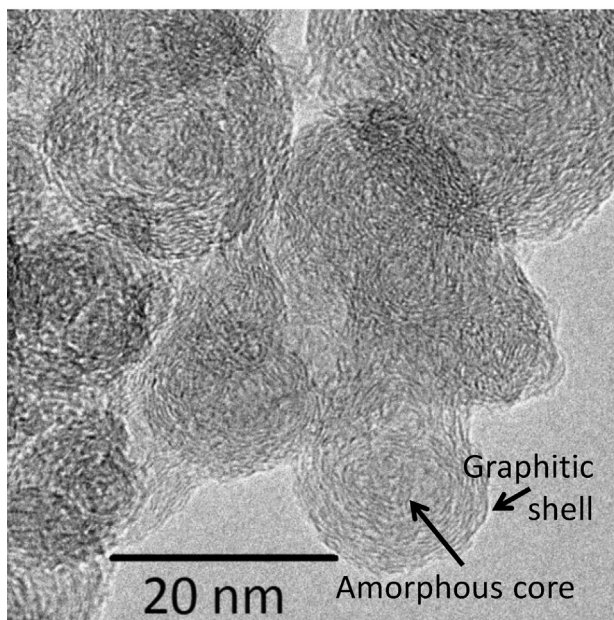
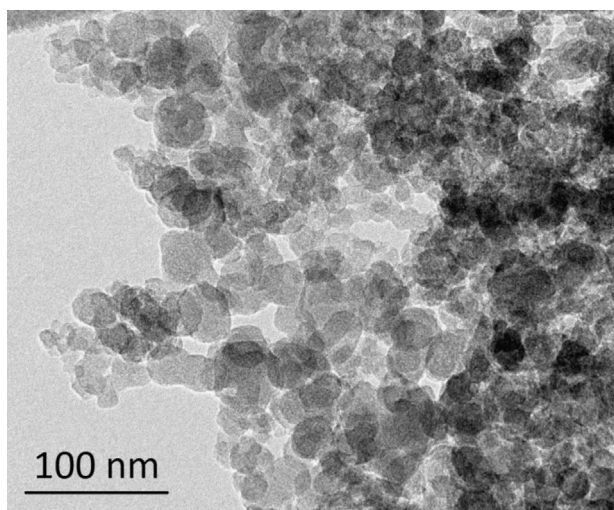
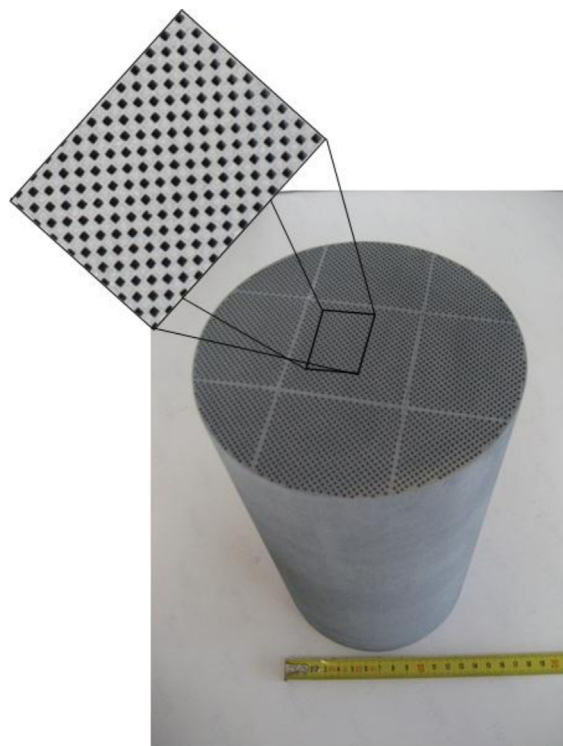
Table 1

Typical Diesel exhaust features measured with a 1600 cc HDI Diesel engine running on commercial Diesel fuel at different rates and with different loadings.

Temperature	<550 °C
[Hydrocarbons]	30–80 ppm
[CO]	200–1500 ppm
[NO]	300–1650 ppm
[NO ₂]	~0 ppm
[O ₂]	5–18%
[H ₂ O]	>2%
[CO ₂]	>2%

needs temperatures above 450 °C, and catalysts play a key role to lower the ignition temperature [6]. The commercially available technologies for filters regeneration are [7]:

- The PSA system: A Ce-fuel additive leads to the formation of CeO₂ particles well embedded into the soot structure, which lower the ignition temperature of soot. Once a high pressure drop is detected by a sensor, fuel is injected and its combustion produces an increase of the exhaust gas temperature that promotes soot ignition. Ceria catalyzes soot combustion and diminishes the

**Fig. 1.** TEM pictures of a real Diesel soot sample.**Fig. 2.** Picture of a commercial SiC Diesel Particulate Filter (DPF).

amount of fuel required for trap regeneration. Recently, iron-based catalysts are being also used.

- The Continuously-Regenerating-Trap (CRT) system (by Johnson Matthey) consists of a wall-flow trap with an upstream flow-through Diesel oxidation catalyst (with Pt) that converts NO to NO₂, which is much more oxidizing than NO and O₂ (and also oxidizes CO and hydrocarbons) and that rapidly reacts with soot.

Both systems work properly, but there are still some aspects to be improved. The main drawbacks of the PSA system is the fuel penalty, which is estimated in about 4%, the CeO₂ deposits on the filter that require periodic cleaning or trap over-sizing, and the high investment costs (additives, additive-storage tank, dosing pump, pressure and temperature sensors, control electronics, etc.). The main drawback of the CRT system is the low sulphur tolerance, and substitution of noble metals by cheaper active phases would be desirable. In addition, in both cases the problem of NO_x emissions remains unsolved.

Some other filters regeneration strategies are being investigated, such as modifications of the CRT systems that incorporate active phases in the filter instead of or in addition to that in the previous oxidation catalyst or the Toyota Motors DPNR (Diesel Particulate NO_x Reduction) system. A number of catalytic active phases are under study in order to develop noble metals-free regeneration strategies and ceria-based materials are among the promising active phases.

2. Why ceria catalysts for soot combustion?

The capacity to store and release oxygen is one of the particular properties of ceria that makes this material exceptionally effective in several catalytic applications [8]. Ceria presents this property due to the ability of cerium to switch between the Ce⁴⁺ and Ce³⁺ oxidation states and to incorporate more or less oxygen into the crystal structure depending on various parameters, such as the gas

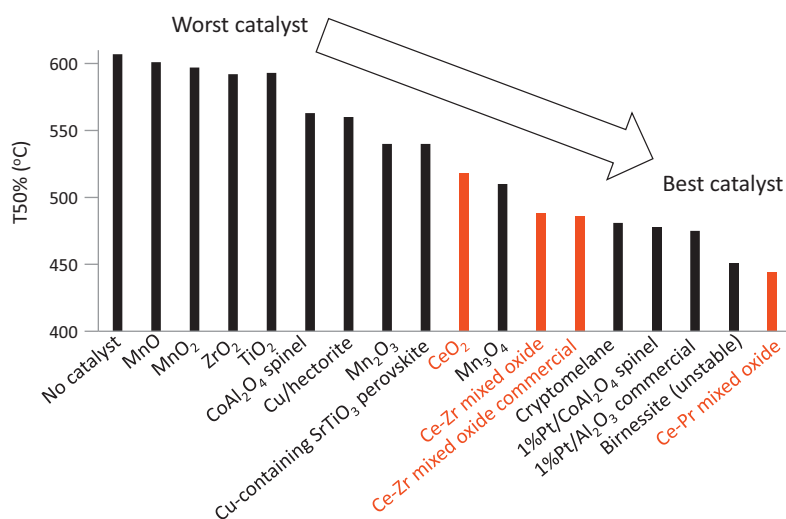


Fig. 3. Potential soot combustion catalysts screening. Experimental conditions: Fixed-bed reactor; soot and powder catalyst mixed in loose contact (with a spatula) in a 1:4 weight ratio; heating at 10 °C/min from room temperature; gas mixture: 500 ppm NO + 5% O₂; 30,000 h⁻¹; model soot: Printex U.

composition, temperature, and pressure. Ceria-based materials are used in Three Way Catalysts (TWC) for gasoline cars pollution control since the mid-1980s [9], being still today one of the main catalytic application of these oxides. The redox properties of the Ce^{3+/4+} couple and the capacity of cerium oxide to exchange oxygen with the gas phase are also behind the good catalytic performance of ceria-based materials as soot combustion catalysts, as it is discussed in the coming sections.

Fig. 3 compares different potential soot combustion catalysts that have been tested in our laboratory under the same experimental conditions (and in some cases have been also prepared, but not always). The results are representative of different types of catalysts, including pure oxides [10,11], platinum [12,13], copper [14–19], zinc [16] and cobalt [12] catalysts, perovskites [14,15,17,19], spinels [13,16], manganese catalysts with birnessite and cryptomelane structure [10,20], alkali [14,17] and alkali earth metals-containing catalysts [15,17,19] and pure and doped cerium oxides [21–31]. The catalysts whose results are included in Fig. 3 are the most active that have been prepared of a particular composition. For instance, during the last six years more than 100 Ce-Zr mixed oxide catalysts have been prepared and tested in our laboratory, and the best result obtained is that included in Fig. 3. Catalytic results available in the literature obtained in other laboratories have not been included in Fig. 3 because an honest comparison is almost impossible, as it is discussed in the next section.

As a general trend, pure oxides that cannot accomplish an oxidation–reduction cycle, like those of titanium, zirconium or manganese (II and IV), have poor or null catalytic activity. Transition metal catalysts such as those of cobalt and copper present activity, but lower to that of Pt. Mixed oxides with cations that can adopt different oxidation states (Mn₃O₄, cryptomelane, pure and doped cerium oxides...) are in some cases as active as soot combustion Pt catalysts, and the most active ceria-based catalyst we have ever prepared, which consists of a high surface area Ce-Pr mixed oxide, is more active than the home-made and commercial Pt-catalysts tested under the experimental conditions of these experiments (see caption of Fig. 3).

Special attention must be paid to alkali metals-containing catalysts. These catalysts are among the most active for soot combustion, but in most cases they are unstable if subjected to high temperature [10,17,32–34]. This is the case, for instance, of the

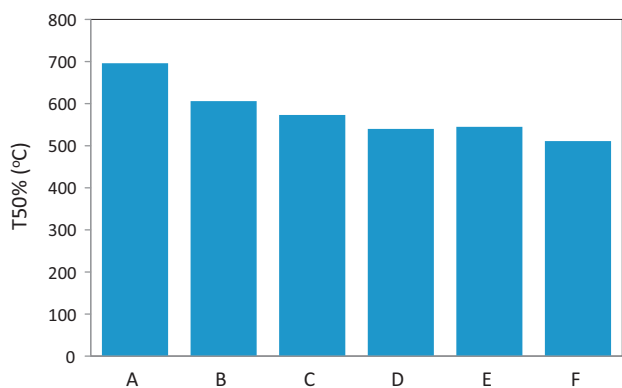
birnessite catalyst included in Fig. 3. Birnessite is a mixed oxide that combines Mn (IV) and Mn (III) cations with alkali and/or alkali earth cations in a laminar structure of [MnO₆] octahedra. This material is the most active manganese catalyst we have ever tested, but the soot combustion mechanism is not really a catalytic process. The mechanistic study suggested that birnessite chemisorbs NO_x (NO_x are always present in Diesel exhausts) and forms potassium nitrate, which melts (melting temperature of KNO₃ is 334 °C) and reacts with soot [10]. This leads to the volatilization of the alkali metal, to the collapse of the structure and to the loss of most activity. Note that carbon (soot) can reduce potassium to the metal state, whose boiling temperature (759 °C) is easily reached during soot combustion. A similar conclusion was achieved during the study of potassium and copper-containing SrTiO₃ perovskites [17]. It was demonstrated that impregnated potassium is progressively lost during the catalytic combustion of soot, and only a minor proportion of the alkali metal, if it is successfully incorporated into the perovskite structure during the synthesis, remains stable under reaction conditions. The catalytic role of such structural potassium is not to act as catalyst itself, but to promote the catalytic activity of the copper-containing perovskite by electronic transfer.

According to the catalysts screening compiled in Fig. 3, ceria-based catalysts are among the most effective for soot combustion, and this has promoted an intense research activity during the last years on different ceria-based catalysts for Diesel soot combustion like, among others, ceria doped with Zr [25,35–38], Fe [36,39], La [21,36,38], Pr [21,36], Sm [21,36], Tb [36], Cu [40–42], Mn [40,43], and Mo [44] and different compounds supported on ceria such as K/Ceria [34,45], Co/Ceria [45–49], Ba,K/Ceria [50,51], Cu-V/Ceria [52], Ag/Ceria [53,54] or Cu/Ceria [55].

3. To be considered for Diesel soot combustion catalysts screening

The soot combustion reaction presents some particular features that must be taken into account for Diesel soot combustion catalysts screening.

The first particular aspect to be taken into account is the type of soot selected to screen catalysts performance. Real soot is heterogeneous, and therefore not convenient for catalysts screening. Depending on the type and age of the engine, running



A: Model soot. Commercial carbon black (Cabot, Vulcan XC-72R)
B: Model soot. Commercial carbon black (Degussa, Printex U)
C and D: Real soots collected in the exhaust of the same engine running in equal conditions with Diesel (C) and bioDiesel (D) fuel.
E and F: Real soots collected in the exhaust of the same engine running in equal conditions before (E) and after (F) a Diesel oxidation catalyst (DOC).

Fig. 4. Temperature for 50% soot combustion (T50%) for different soot samples. Experimental conditions: Fixed-bed reactor; no catalyst; heating at 10 °C/min from room temperature; gas mixture: 500 ppm NO_x + 5% O₂; 30,000 h⁻¹.

conditions, type of oil and fuel used, etc. important differences in the amount and type of ashes (sometimes metals with potential catalytic activity), amount of adsorbed hydrocarbons (from 5% to 60% [56]) and degree of graphitization of the soot formed can be found [6,14,57,58]. As an example, Fig. 4 compiles combustion results of several model and real soot samples where these differences are evidenced. For more details about the physicochemical properties of these soot samples the reader is referred to the original sources [6,14]. Due to the heterogeneous nature of real soot, commercial carbon blacks are usually preferred as model soot for catalysts screening, and Printex U (Evonik-Degussa GmbH) is a quite popular reference material.

Another aspect to be considered for soot combustion catalysts screening is the soot-catalyst contact, which significantly affects the results of catalytic combustion experiments. In a real catalyst containing-DPF fitted in the exhaust pipe of a Diesel vehicle the soot-catalyst contact is assumed to be poor, and the challenge is how to mimic such contact in laboratory experiments with powder catalysts. Van Setten et al. [58] evaluated different methods for bringing the soot in physical contact with a powder catalyst in order to determine which methods give a realistic contact. Their conclusion was that suitable methods are filtration from an (artificial) soot aerosol with a catalyst-containing filter, shaking soot and powder catalyst in a bottle, mixing soot and powder catalyst with a spatula, and dipping the catalyst-containing filter in a soot dispersion. On the contrary, intimate mixtures of soot and powder catalyst like mixing in a ball milling or in a mortar provide meaningless catalytic results from a practical point of view. As an example, Fig. 5 presents the soot conversion curves obtained with a ceria catalyst mixed in loose (with a spatula) and tight (in a mortar) contact with soot. A ceria catalyst with very poor activity was selected (ceria calcined at 1000 °C) for these experiments in order to evidence that a significant decrease in the soot conversion curve with regard to the uncatalyzed reaction is obtained with the tight contact mixture while such decrease is almost null with the loose contact mixture.

One more particular feature of the soot combustion reaction that must be taken into consideration for catalysts screening is that the

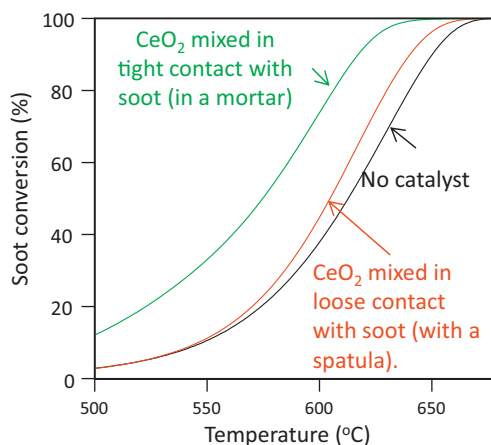


Fig. 5. Effect of soot-catalyst contact in ceria-catalyzed soot combustion. Experimental conditions: TGA reactor; soot:catalyst weight ratio 1:4; heating at 10 °C/min from room temperature; gas mixture: air; model soot: Printex U; ceria catalyst preparation: cerium nitrate was calcined at 1000 °C.

properties of soot (amount of oxygen, size and shape of the particles, graphitic structure, surface area, and so on) change during the combustion, and therefore, the kinetic parameters (reaction rates, activation energies, pre-exponential factors, ...) depend on the soot conversion degree. This is evidenced in Fig. 6, where the combustion rates during two ceria (bare and 5 wt.% La doped)-catalyzed soot combustion experiments are plotted against the soot conversion percentage. In both profiles, the combustion rate increases rapidly once the oxidizing gas mixture is fed to the reactor, showing a narrow peak below 10% soot conversion. This narrow peak is attributed to the fast combustion of the absorbed hydrocarbons which were not evolved during the previous heating step in inert flow and/or to the initial attack of the oxidizing gases to surface carbon atoms that became unsaturated and highly reactive upon surface oxygen groups release while heating in inert gas. After these early peaks, the reaction rate rises smoothly until 80–90% soot conversion, evidencing that soot becomes progressively more reactive, and the reaction rate increases out of control at the end of the combustion. Due to this change in the combustion rates with the soot conversion degree the kinetic parameters, which are the best way to compare catalysts performance in most catalyzed reactions, are only valid for very particular soot combustion conditions. This

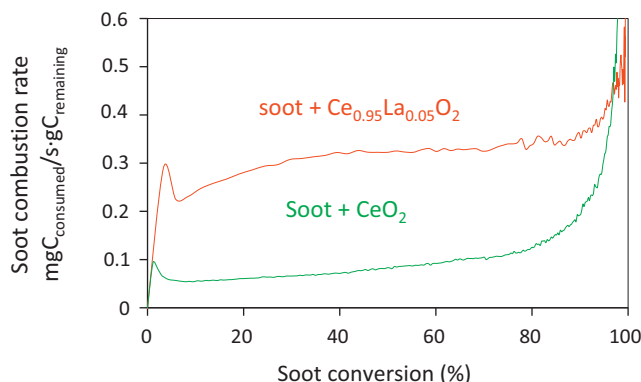


Fig. 6. Two examples of ceria (bare and La-doped) catalyzed soot combustion rates. Experimental conditions: Fixed-bed reactor; soot and powder catalysts were mixed in loose contact (with a spatula) in a 1:4 weight ratio; the soot-catalyst mixtures were heated in N₂ flow until 450 °C, and the inert gas was then replaced by a 500 ppm NO + 5% O₂ mixture, keeping the same temperature (450 °C) until total soot combustion. 30,000 h⁻¹ Model soot: Printex U. Catalysts preparation: cerium nitrate and an intimate mixture of cerium nitrate and lanthanum nitrate were calcined at 1000 °C.

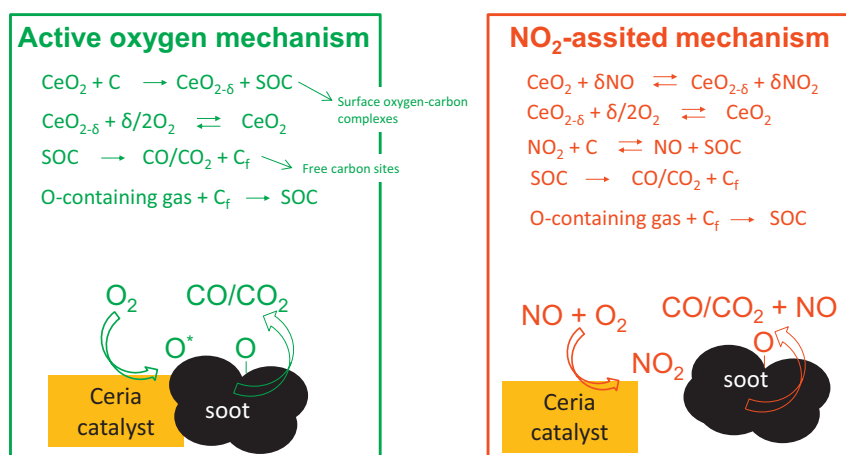


Fig. 7. Scheme of the potential ceria-catalysed soot combustion mechanisms.

handicap has motivated that, in most articles devoted to the study of soot combustion catalysts, combustion experiments consist of heating soot-catalyst mixtures at a fixed rate (instead of isothermal reactions) and parameters like the T50% (°C) (temperature required to combust 50% of soot in a particular reaction conditions), T_{onset} (°C) (soot combustion onset temperatures) or some others equivalent, are adopted as comparison criteria. This type of parameters have the same limitations than the kinetic parameters (are only valid for very particular reaction conditions) but are determined more easily.

4. Ceria-catalyzed Diesel soot combustion mechanisms

Before describing in detail the role of ceria catalysts in Diesel soot combustion, it is useful to revisit previous literature related with carbon materials gasification [59–61,56], like coal gasification or activation of carbon materials, since there are many points in common with Diesel soot combustion. Moulijn and Kapteijn [61] proposed a unified theory to explain the reaction of carbon with oxygen-containing molecules. In the formulation of this theory the reactions of O_2 , H_2O , CO_2 , NO and N_2O with carbon were considered, and proposed that at least two steps take place in all cases: the transfer of oxygen atoms from the gas phase molecules to the carbon surface, with the creation of surface oxygen complexes (SOC) [62], and the decomposition of these surface oxygen complexes with CO and/or CO_2 release. It was also proposed that the decomposition of these surface oxygen complexes leaves highly reactive carbon atoms (C_f : free carbon site) with unsaturated valences at the carbon surface where further oxidizing molecules will preferentially react. These general reaction steps also take place during Diesel soot combustion.

In a real Diesel engine exhaust there are several oxygen-containing gas molecules that could potentially react with soot (see Table 1): O_2 , NO , H_2O and CO_2 . The reactivity of H_2O , CO_2 and NO is too low to directly react with soot at typical temperatures of Diesel exhausts, O_2 being the only reactive enough gas to oxidize Diesel soot in some conditions. In addition, NO can be catalytically oxidized to NO_2 , which is more reactive than NO and O_2 . As mentioned in the introduction, the CRT system is based on the catalytic oxidation of NO to NO_2 by a Pt catalyst. Summing up, in a real DPF filter soot combustion is mainly oxidized by NO_2 and/or by O_2 , and two ceria-catalyzed combustion mechanisms have been identified, the so-called “ NO_2 assisted mechanism” and the “active oxygen mechanism”. A scheme of both mechanisms is included in Fig. 7 together with the main steps involved in each case.

As an example, Fig. 8 shows soot conversion profiles obtained in ceria-catalyzed combustion experiments performed at laboratory with two gas streams: 5% O_2 in N_2 and 500 ppm $\text{NO} + 5\%\text{O}_2$ in N_2 , where it is demonstrated that ceria is able to accelerate soot combustion either with O_2 and with NO_x/O_2 . As expected, ceria-catalyzed soot combustion with $\text{NO} + \text{O}_2$ occurs at lower temperatures than the ceria-catalyzed O_2 combustion due to the participation, as it will be next discussed, of the NO_2 molecule.

4.1. Active oxygen mechanism

In the O_2 -rich gas streams of Diesel-engines exhausts, ceria is able to exchange its oxygen with gas-phase O_2 [63]. During this exchange process highly reactive oxygen species are created (the so-called “active oxygen”), which can be involved in different catalytic processes. The highly reactive active oxygen atoms can oxidize soot very efficiently. As an example, Fig. 9 shows results of a TAP experiment consisted of pulsing a very small amount of gas ($\sim 10^6$ molecules of Ar or $^{18}\text{O}_2$) over a tight mixture of soot and ceria ($\sim 10^{20}$ ceria molecules). Part of the $^{18}\text{O}_2$ pulsed was consumed (the area under its profile is smaller to that of the reference Ar pulse) and C^{16}O and C^{16}O_2 evolved. This evidenced that soot was oxidized by catalyst oxygen (^{16}O) and that the $^{18}\text{O}_2$ consumed was captured by the ceria catalyst to restore the oxygen balance.

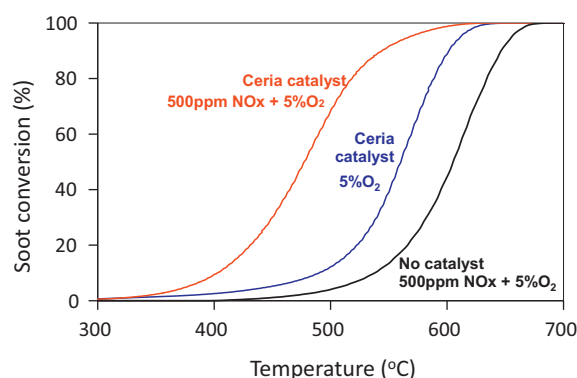


Fig. 8. Uncatalyzed and ceria-catalyzed soot combustion with O_2 and $\text{NO} + \text{O}_2$. Experimental conditions: Fixed-bed reactor; soot and powder catalysts were mixed in loose contact (with a spatula) in a 1:4 weight ratio; heating at $10^\circ\text{C}/\text{min}$ from room temperature; gas mixtures: 5% O_2/N_2 and 500 ppm $\text{NO} + 5\%\text{O}_2$ in N_2 ; model soot: Printex U.

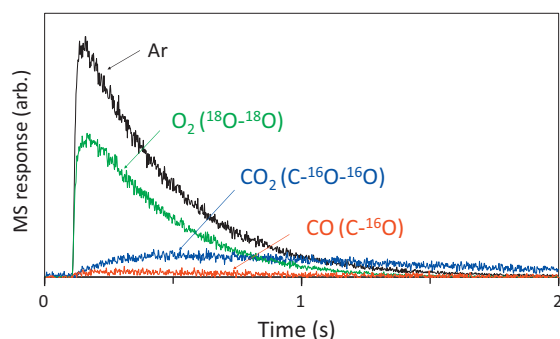


Fig. 9. Ar and $^{18}\text{O}_2$ pulses over a soot-ceria mixture at 400 °C in a TAP reactor. Experimental conditions: soot and powder ceria catalyst were mixed in tight contact (in a mortar) in a 1:10 weight ratio; model soot: Printex U. Catalyst preparation: cerium nitrate was calcined at 1000 °C.

Table 2

Activation energies determined by Otszawa method for 50% soot conversion (KJ/mol) without and with ceria catalysts. Experimental conditions: TGA reactor; soot:catalyst weight ratio 1:4 mixed in tight contact; Heating at different rates from room temperature; gas mixture: air; model soot: Printex U; Catalysts preparation: cerium nitrate and an intimate mixture of cerium nitrate and lanthanum nitrate were calcined at 600, 800 or 1000 °C.

Catalyst formulation	Catalyst calcination temperature (°C)	Activation energy determined by Otszawa method for 50% soot conversion (KJ/mol).
No catalyst	–	151
CeO ₂	600	149
CeO ₂	800	142
CeO ₂	1000	176
Ce _{0.9} La _{0.1} O ₂	600	162
Ce _{0.9} La _{0.1} O ₂	800	172
Ce _{0.9} La _{0.1} O ₂	1000	168

The activation energies of the uncatalyzed and ceria-catalyzed soot–O₂ reaction were determined by the Ozawa method [64–66] for several ceria catalysts (pure and La-doped cerias calcined at 600, 800 and 1000 °C) and for 50% soot conversion, and the results obtained are included in Table 2. The activation energies both for the uncatalyzed and catalyzed reactions were in the range 142–176 kJ/mol and values above 100 kJ/mol have been related to the dissociative chemisorption of O₂ on carbon sites [67] and, in the case of catalyzed reactions, to the interaction between catalyst and carbon surface [68]. These activation energy values also supported that the role of the ceria catalysts is to promote the transfer of oxygen from the gas phase to the carbon surface.

The feasibility of the active oxygen soot combustion mechanism strongly depends on the soot-ceria contact. The lifetime of active oxygen has not been reported, but oxygen exchange experiments performed in a TAP reactor suggest that whether there is not contact between soot and catalyst two active oxygen atoms released from ceria recombine to each other and yield O₂ again [63].

4.2. NO₂-assisted mechanism

If temperature is high enough (roughly above 300 °C) ceria is able to catalyze the oxidation of NO to NO₂, and NO₂ is much more oxidizing than O₂ and NO and can initiate soot combustion. Once NO₂ reacts with soot the remaining part of the mechanism is not that different to that described for “active oxygen” (see scheme in Fig. 7). The surface oxygen–carbon complexes created upon NO₂ oxidation decompose and yield CO/CO₂ and the free carbon sites created on the surface will be suitable to chemisorb further oxidizing molecules. Taking into account that O₂ is the most abundant O-containing gas in a Diesel exhaust it is expected that it will

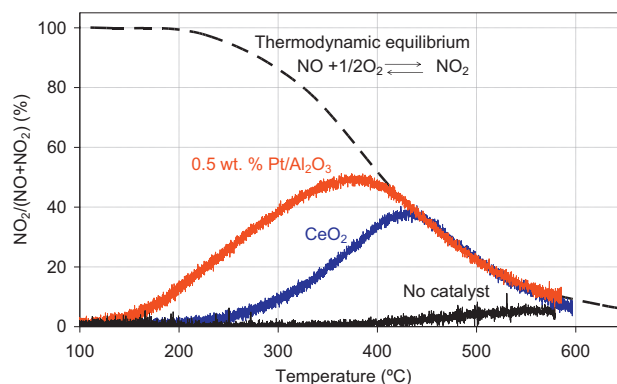


Fig. 10. Uncatalyzed and catalyzed NO oxidation to NO₂. Experimental conditions: Fixed-bed reactor; heating at 0.6 °C/min from room temperature; gas mixtures: 600 ppm NO + 10%O₂ in N₂; 70,000 h^{−1}; Ceria catalyst preparation: cerium nitrate was calcined at 600 °C; Pt catalyst preparation: γ-alumina impregnation with an aqueous solution of tetraammineplatinum(II) nitrate and calcination at 500 °C.

contribute significantly to soot combustion even in the NO₂-assisted mechanism, once the soot combustion has started [69].

The ceria catalyzed NO₂-assisted mechanism is similar to that described for Pt catalysts in the CRT system (see introduction). As an example, Fig. 10 shows NO oxidation laboratory experiments performed with model Pt and ceria catalysts. Both profiles are qualitatively similar. Above a certain temperature NO is progressively oxidized to NO₂ until a maximum level is achieved, and above this maximum the NO₂ level decreases following the thermodynamic profile of the NO/NO₂ equilibrium. Due to this equilibrium, the mixtures of NO + NO₂ are generically referred to as NO_x, since the proportion of NO and NO₂ changes depending on temperature, pressure, presence of catalysts, time of NO + O₂ contact (if there is O₂ available).

Taking into account the NO₂ profiles included in Fig. 10 it can be explained why soot combustion ceria catalysts are as effective (and even more in some cases) as Pt catalysts (see Fig. 3). Differences between ceria and Pt catalyzed NO₂ production profiles (Fig. 10) are only important before the thermodynamic equilibrium of the NO/NO₂ reaction is achieved but, since the thermodynamic threshold cannot be overcome, both profiles are equal above a certain temperature (420 °C in the experimental conditions of Fig. 10). At typical soot combustion temperatures the thermodynamic equilibrium is achieved both by Pt and ceria, and the only difference is the number of times that every NO molecule can be oxidized to NO₂ (the NO₂–soot reaction yields NO again) during the time they are in contact with the soot-catalyst mixture. Since GHSV values are typically high in a real Diesel engine (typically 30,000–100,000 h^{−1}, depending on the running conditions) such recycling of NO only occurs few times. In conclusion, at typical soot combustion temperatures in a Diesel exhaust the amount of NO₂ produced by Pt and ceria catalysts is quite similar because it is limited by thermodynamics. If the “NO₂-assisted” mechanism prevails, a good ceria catalyst (in the next sections it is discussed what is a good ceria catalyst) and a Pt catalyst have the same effect on soot combustion, and if the ceria catalyst is designed to promote significantly the “active oxygen” mechanism (Pt has not this chance), ceria can be even more effective than Pt.

Finally, Fig. 11 shows a clear example of a set of ceria catalysts where the “NO₂-assisted” soot combustion mechanism prevails. In this figure is plotted the maximum level of NO₂ reached by each ceria catalyst in oxidation experiments performed with a NO + O₂ mixture in the absence of soot and the temperature for 50% soot conversion in soot combustion experiments performed with the same gas mixture. A clear relationship between NO₂ production

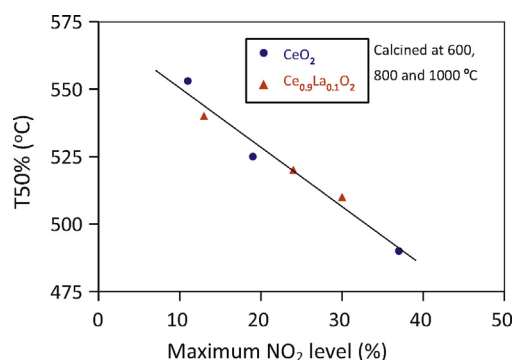


Fig. 11. Relationship between ceria-catalyzed NO oxidation to NO₂ and soot combustion (T50% parameter). Experimental conditions: Fixed-bed reactor; heating at 0.6 °C/min from room temperature; gas mixtures: 600 ppm NO + 10% O₂ in N₂; 70,000 h⁻¹; catalysts preparation: cerium nitrate and an intimate mixture of cerium nitrate and lanthanum nitrate were calcined at 600, 800 or 1000 °C; model soot: Printex U.

and soot combustion is shown, evidencing that the combustion of soot mainly occurs throughout the NO₂-assisted mechanism.

5. Doped ceria better than bare

It is well known that doping ceria with proper foreign cations has different benefits on the catalytic features of this material, improving the thermal stability, surface reducibility, oxygen storage capacity, oxygen mobility within the framework, etc. [70].

Diesel soot combustion is a demanding application due to the high temperatures achieved during soot combustion. The temperature inside the filter can increase up to 1000–1100 °C, and even more in particular hot spots, as a consequence of the highly exothermal soot combustion process. Gradients on the filters of 100 °C/cm along both radial and longitudinal directions have been reported [5]. For this reason, the main goal of soot combustion ceria catalysts doping is to improve thermal stability, despite other ceria properties could also change upon doping.

As an example of the effect of temperature on the catalytic activity for soot combustion of pure and doped cerias, Fig. 12 shows soot conversion profiles obtained with three bare ceria catalysts calcined at 600, 800 and 1000 °C and with three Ce_{0.9}La_{0.1}O₂ catalysts calcined at the same temperatures. The catalytic activity of both formulations decreases with the calcination temperature, but while bare ceria becomes almost inactive upon calcination at 1000 °C, Ce_{0.9}La_{0.1}O₂ keeps certain activity after such severe thermal aging.

Thermal aging of ceria materials has several negative effects on their physicochemical properties. Sintering is one of the effects of temperature, as observed in the TEM images of Fig. 13. In this figure pictures of bare and 10% La-doped ceria calcined at 600 and 1000 °C are observed. The crystals of both catalysts calcined at 600 °C are quite similar, with size of few nanometers. However after calcination at 1000 °C the crystals of bare ceria grow until more than 50 nm while those of La-doped ceria keep sizes smaller than 30 nm.

The redox properties of ceria catalysts are also significantly affected by temperature. This is evidenced in Fig. 14, where the reduction profiles of the bare and La-doped ceria catalysts tested in Fig. 12 are compiled. In these profiles, H₂ consumption must be attributed to the reduction of Ce⁴⁺ to Ce³⁺, because La³⁺ is a non-reducible cation. The H₂ reduction profile of pure ceria calcined at mild temperature (600 °C in the example of Fig. 14) typically presents two peaks, one of them at around 450 °C, which is attributed to surface reduction, and another one at around 850 °C, which is assigned to bulk reduction [71]. As observed in Fig. 14, the surface reduction peak of pure ceria diminishes with

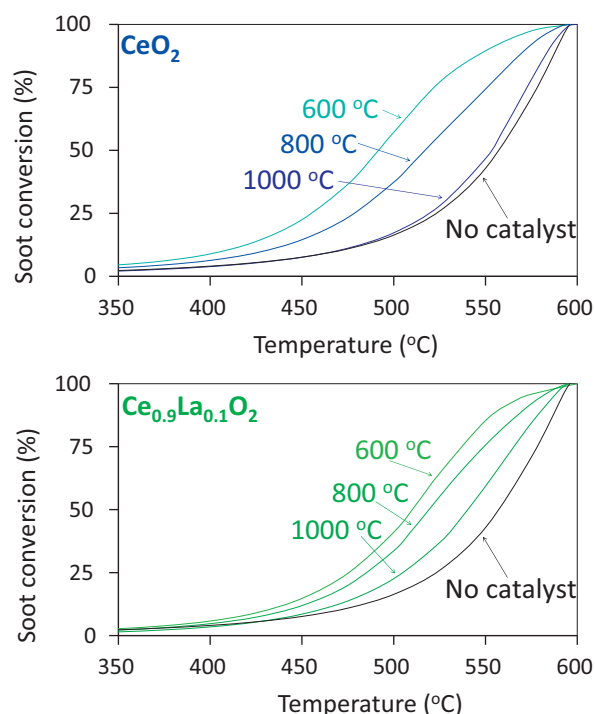


Fig. 12. Effect of catalyst thermal aging on pure and La-doped ceria-catalysed soot combustion. Experimental conditions: Fixed-bed reactor; heating at 0.6 °C/min from room temperature; gas mixtures: 600 ppm NO + 10% O₂ in N₂; 70,000 h⁻¹; catalysts preparation: cerium nitrate and an intimate mixture of cerium nitrate and lanthanum nitrate were calcined at 600, 800 or 1000 °C; model soot: Printex U.

calcination temperature due to sintering, that is, because of crystal growth and surface area decrease.

The H₂ reduction profiles of doped cerias are usually different to those of bare ceria, as observed in the profiles of Ce_{0.9}La_{0.1}O₂ included in Fig. 14. Typically, doped cerias do not show the surface and bulk reduction peaks but a broad band in a very wide range of temperature. This type of profile is a consequence of the high mobility of oxygen within the lattice [71], since once the surface oxygen is reduced bulk oxygen migrates rapidly to surface and the reduction continues.

The effect of high temperature aging on doped cerias reducibility is not as dramatic as in bare ceria, as observed in Fig. 14 for Ce_{0.9}La_{0.1}O₂. The doped ceria catalyst keeps certain surface reducibility and good oxygen mobility between bulk and surface even after 1000 °C calcination.

XRD is also a sensible technique to changes on ceria-based catalysts due to high temperature aging, as it is observed in Fig. 15 for pure and 10% La doped ceria. The XRD peaks of both catalysts become narrower and more intense progressively with temperature, evidencing better crystalline order. From the X-ray diffractograms, the average crystal size of the ceria catalysts can be estimated with different models, as the Williamson-Hall equation [72], which is quite convenient to be applied to doped cerias because separates the effects of size and strain in the crystals on the XRD peaks width. The average crystal size estimated from XRD patterns is included in Fig. 16 for pure ceria calcined at temperatures between 500 and 1000 °C and for Zr, La or Pr doped ceria, also calcined at several temperatures. The crystal size of pure ceria grows rapidly from 500 °C, while the size of the doped ceria grows much more smoothly or remains even constant in a wide range of temperatures.

All results presented in this section till now have evidenced that ceria doping with suitable cations like Zr, Pr or La has a positive effect on soot combustion ceria catalyst, mainly improving the

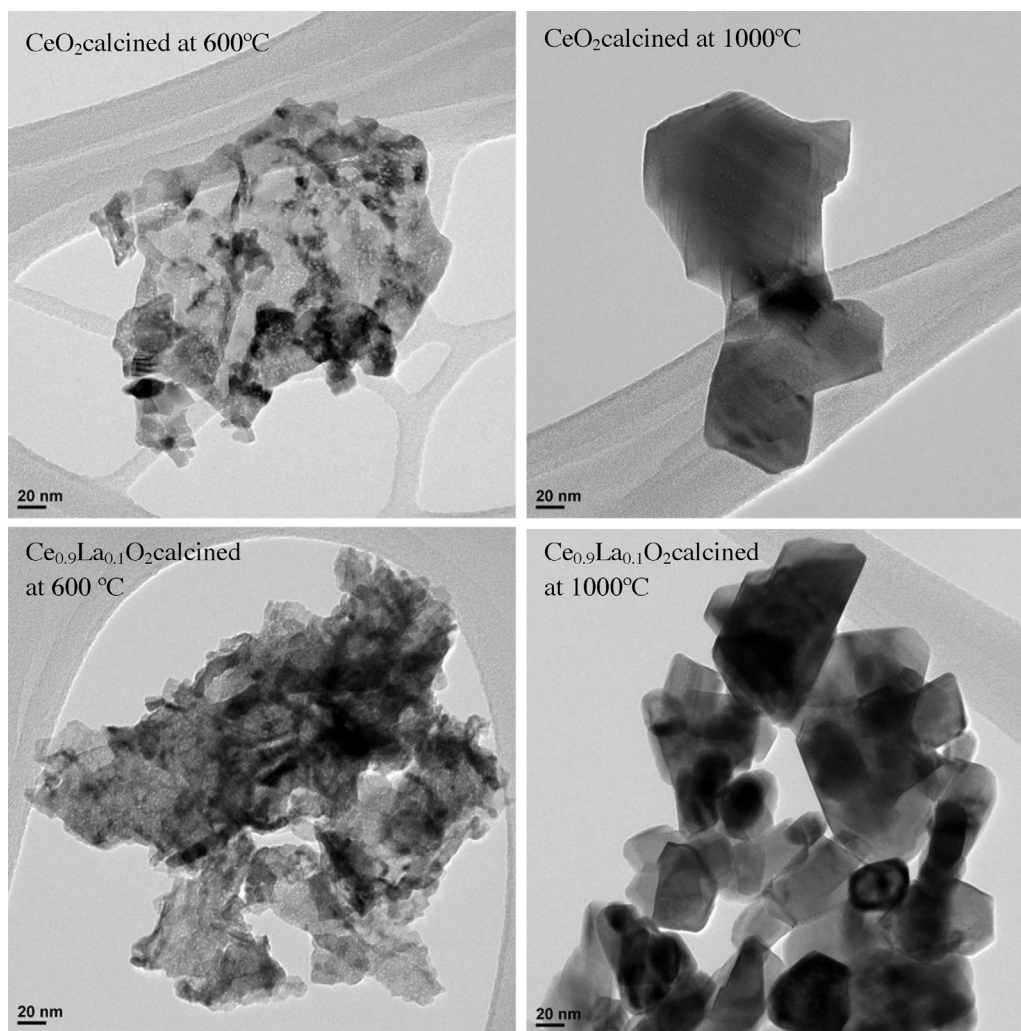


Fig. 13. TEM images of bare and La-doped ceria catalysts calcined at 600 and 1000 °C.

thermal stability of ceria. This improvement is mainly evident if pure and doped ceria catalysts calcined at high temperature are compared. However, the introduction of foreign cations on ceria also affects in somehow the chemical behavior of the catalyst even when calcined at mild temperatures. For instance, the curves on

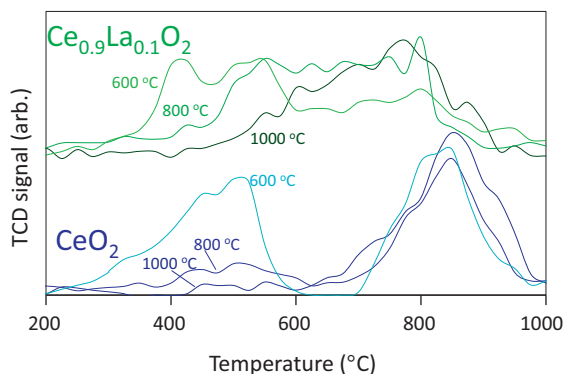


Fig. 14. Effect of temperature on pure and La-doped ceria catalysts reducibility studied by H₂-TPR. Experimental conditions: Fixed bed reactor coupled to a TCD analyzer; 50 mg of catalyst were heated at 10 °C/min from room temperature in 30 ml/min flow of 7.7 vol% H₂/Ar; catalysts preparation: cerium nitrate and an intimate mixture of cerium nitrate and lanthanum nitrate were calcined at 600, 800 or 1000 °C.

Fig. 12 shown that CeO₂ calcined at 600 °C is more active for soot combustion than Ce_{0.9}La_{0.1}O₂ calcined at the same temperature, indicating that La-doping has a positive effect on ceria behavior for high temperature calcined catalyst but not for catalysts calcined at mild temperatures. This different effect of dopants depending on the calcination temperature has not been studied in detail for most dopants, but a detailed analysis was done for Zr-doped ceria

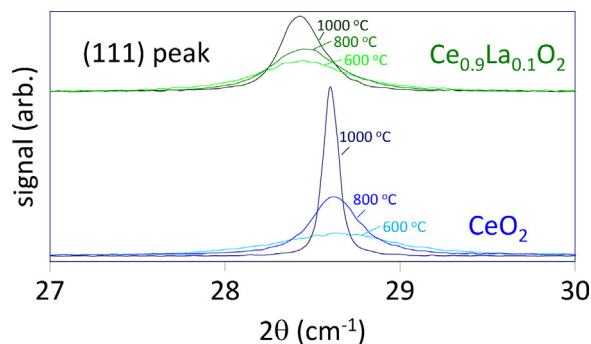


Fig. 15. Effect of temperature on pure and La-doped cerias characterized by XRD (detail of the 1 1 1 (peak)). catalysts preparation: cerium nitrate and an intimate mixture of cerium nitrate and lanthanum nitrate were calcined at 600, 800 or 1000 °C.

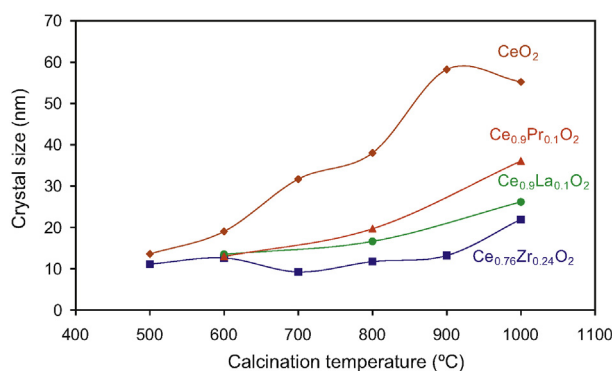


Fig. 16. Effect of temperature on pure and doped ceria crystal size. Pure ceria and Ce-Zr mixed oxides were prepared by (co-)precipitation with ammonia and calcination, and the remaining mixed oxides were prepared by calcination of a tight mixture of the nitrate precursors. Crystal sizes were determined from XRD patterns with the Williamson-Hall equation.

[27]. As an example, the double role of ceria doping with Zr is now discussed for catalysts calcined at 600 °C.

Fig. 17 shows a linear relationship between ceria-catalyzed NO oxidation to NO₂ and soot combustion (T50% parameter) for a set of Ce_xZr_{1-x}O₂ ($1 \geq x \geq 0.2$) catalysts. This relationship means that the prevailing mechanism for this set of catalysts tested under the experimental conditions of these experiments is the NO₂-assisted mechanism. In Fig. 18, the maximum NO₂ level achieved by each catalyst has been plotted against the cerium content, and all mixed oxides follow a linear trend while pure ceria NO₂ level lies below the expected value considering this trend. Therefore, the amount of cerium is the parameter controlling the NO₂ production by Ce-Zr mixed oxides, and at the end the combustion of soot, but the intrinsic activity for NO oxidation to NO₂ of cerium in the pure oxide is lower to that in the Ce-Zr mixed oxides. The effect of Zr doping on cerium catalytic performance was studied by in situ DRIFTS and by NO_x adsorption and further He-TPD [27] and it was concluded that, in a first step, surface nitrites are formed upon Ce-Zr mixed oxides interaction with NO + O₂. These nitrites are progressively converted to nitrates, and NO₂ is yielded after these adsorption/oxidation/desorption processes. It was concluded that ceria doping by Zr improves the surface oxidation of nitrites (cerium oxidizes surface nitrites faster when doped by Zr). However, the production of NO₂ in the range of temperatures relevant to soot oxidation not only depends on the NO/nitrites oxidation capacity of the

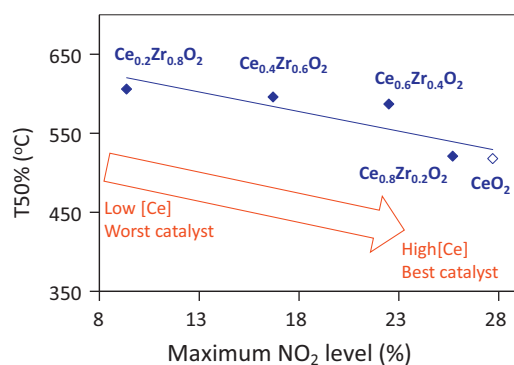


Fig. 17. Relationship between ceria-catalyzed NO oxidation to NO₂ and soot combustion (T50% parameter) for a set of Ce_xZr_{1-x}O₂ ($1 \geq x \geq 0.2$) catalysts. Experimental conditions: Fixed-bed reactor; heating at 10 °C/min from room temperature 500 ppm NO + 5%O₂ in N₂; soot and powder catalysts were mixed in loose contact (with a spatula) in a 1:4 weight ratio; model soot: Printex U; maximum NO₂ levels were determined in similar experiments conditions but only with catalyst (without soot); catalysts were prepared by (co-)precipitation with ammonia and calcination at 500 °C.

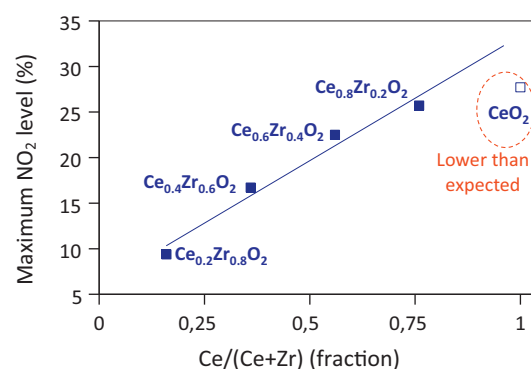


Fig. 18. Relationship between amount of ceria in a set of Ce_xZr_{1-x}O₂ ($1 \geq x \geq 0.2$) catalysts and catalytic oxidation of NO to NO₂. Experimental conditions described in caption of Fig. 17.

catalyst but also on the adsorption strength of the nitrates under NO oxidation conditions, and the thermostability of the nitrates adsorbed on zirconium sites is higher than that of nitrates adsorbed on cerium sites. In conclusion, Zr cations doping ceria have a double role on the catalytic oxidation of NO to NO₂: (i) Zr enhances the oxidation rate of the adsorbed nitrates but (ii) stabilizes the oxidized species and hinders NO₂ release. This process is summarized in the scheme of Fig. 19.

Finally, great research efforts have been done in order to determine which properties of pure and doped ceria are the most critical for Diesel soot combustion application, but there is not a clear consensus about it. BET surface area, crystal size, oxygen storage capacity, surface reducibility, and surface composition have been reported to affect the catalytic activity for soot combustion under certain experimental conditions used in laboratory experiments [21,25,29,36]. However, in the Diesel soot combustion application, it is difficult to reach an agreement about which property is the most critical one, because the answer to this question depends on the experimental conditions used to perform the catalytic tests, that is, the soot-catalyst contact mode (loose or tight), the gas composition (only with O₂ or also with NO_x), the nature of soot, the set of ceria catalysts compared, the type of reactor (TGA, flow reactor, etc.), the prevailing combustion mechanism (NO₂-assisted or active oxygen-assisted) and so on. However, some general conclusions can be drawn:

- High surface area/small crystal size of ceria usually has a positive effect since there is more surface available to catalyze the oxidation of NO to NO₂ and more contact points with soot to transfer active oxygen.
- In mixed oxides, the composition [23,25,27,36] (and in particular the surface composition [29]) is always a key feature, and the optimal composition depends on the foreign cation. For instance, the optimum loading for La³⁺, Zr⁴⁺, and Pr^{3+/4+}-doping are around 5–10% [63], 20–30% [25,36] and 50 mol% [23] respectively, and this optimum loading depends on the dopant size and on its redox properties.

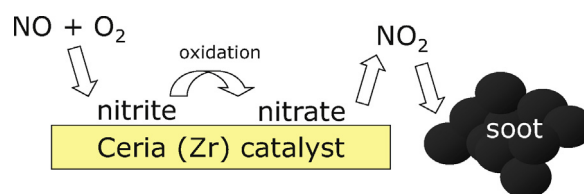


Fig. 19. Simplified scheme of the processes occurring on a (Zr-doped) ceria catalyst surface during the catalytic oxidation of NO to NO₂ and further oxidation of soot by NO₂.

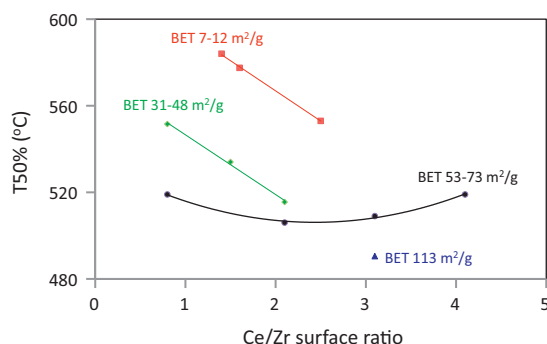


Fig. 20. Effect of the surface properties of a set of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ mixed oxides (prepared by different methods) on the catalytic combustion of soot.

- Most authors conclude that the surface properties are more important than those of the bulk [29,73]. For instance, the oxygen storage capacity, which involves bulk oxygen, seems to be only important in the absence or defect of gas-phase O_2 , but not in O_2 -rich environments [73].

The important role of surface properties of ceria catalysts on soot combustion is supported by the results included in Fig. 20, where it is also evidenced that is not possible to select a single property to explain the activity. For instance, for the set of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ catalysts included in Fig. 20, which were prepared by different methods [29], the amount of ceria on surface seems to play a key role – the higher the better – if catalysts with similar and not too high BET surface area are compared (see series with BET 7–12 m^2/g and 31–48 m^2/g). However, if BET area is higher (53–73 m^2/g) the surface concentration of ceria is not important, and if samples with the same Ce/Zr ratio are compared the BET area is a critical parameter. In conclusion, the catalytic activity for soot combustion of ceria-based catalysts mainly depends on the surface properties (area and composition) of the catalysts.

6. Conclusions

In this review article different aspects of the ceria-catalyzed Diesel soot combustion reaction have been critically discussed, and the following general conclusions can be summarized:

- Two potential ceria-catalyzed soot combustion mechanisms have been identified, the so-called active oxygen mechanism and the NO_2 -assisted mechanism.
- Ceria must be doped with a foreign cation, like those of Zr, La or Pr, to enhance thermal stability.
- Ceria doping not only affects thermal stability but also changes different physicochemical and catalytic properties of ceria. Zr-doping, for instance, has a double role on ceria as soot combustion catalyst: enhances ceria oxidation capacity of the adsorbed NO_x species (positive effect) but stabilizes NO_2 on surface (negative effect).
- The surface properties of a ceria catalyst are usually more important than those of bulk: high surface area/small crystal size usually has a positive effect on the catalyst performance and, in mixed oxides, the surface composition also plays a role.
- The optimal dopant loading depends on the foreign cation being, for instance, around 5–10%, 20–30% and 50 mol% for La^{3+} , Zr^{4+} , and $\text{Pr}^{3+/4+}$, respectively.

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